



Letter to the Editors

Determination of the lithium diffusion coefficient in irradiated boron carbide pellets

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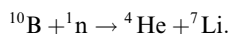
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Abstract

During neutron irradiation, ^{10}B atoms in B_4C are destroyed, producing lithium and helium atoms according to the well-known $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. The aim of this work is to measure the lithium diffusion coefficient of high density boron carbide material. The nuclear microprobe technique is used to determine lithium concentration profiles in irradiated B_4C pellets. The analysis of the measured lithium concentration profiles allows to calculate a lithium diffusion coefficient in this material. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Boron carbide is one of the most universal compounds used for the control and shutdown of nuclear reactor plants. Under neutron irradiation, ^{10}B atoms capture neutrons according to the reaction



Many authors [1,2] have investigated the role of helium in the structure of the boron carbide, but only few contributions refer to the lithium behavior. Hollenberg and Cumming [3] have expressed the idea that the substitution or the interstitial incorporation of lithium in the structure is possible, but they have observed that there is no experimental data concerning the lithium solubility in boron carbide. Stoto and Housseau [4] have shown that lithium does not change the crystallographic structure of B_4C unit cells (no variation of the cell parameters or of the cell volume have been observed) and does not precipitate. In a previous work [5], we have shown that lithium can migrate out of boron carbide pellets during neutron irradiation. The lithium loss is very low for dense pellet operating in fast breeder reactors (FBR) conditions, but it is more important for low density pellets operating in pressurized water reactors (PWR) conditions. In order to quantify the migra-

tion of lithium atoms, it is necessary to determine the lithium diffusion coefficient in B_4C . Kervalishvili [6] has investigated the effect of lithium on dimensional and phase stability of hot-pressed boron carbide. He has also estimated the lithium diffusion coefficient in unirradiated B_4C material. To determine this coefficient, high density B_4C samples were heated with a batch of metallic lithium. The depth and front of lithium penetration into B_4C have been measured in previous investigations by means of a scanning electron microscope. Instead of using such a method, we have analyzed the lithium concentration of irradiated B_4C samples in a FBR (Phenix) after and before different annealing, by means of the nuclear microprobe technic. The objective of this work is to determine the lithium diffusion coefficient in these samples.

2. Experimental procedure

Cylindrical specimens of boron carbide with a density of 2.4 g/cm^3 (96% of the theoretical density) were obtained by vacuum hot pressing of pure boron carbide powder ($\text{B} + \text{C} = 98.6\% \text{ wt.}$). The grain size of the pellets is lower than $10 \mu\text{m}$. These materials have been irradiated into the Phenix reactor. The pellets (height of 11 mm, and diameter (D) of 6.6 mm) were stacked in a stainless steel sheath and directly cooled by the liquid sodium. The surface temperature of the pellets was around 510°C . Owing to their small dimensions and to the fast neutron flux, the ^{10}B atoms capture profile is

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Table 1
Annealing temperatures, annealing times and lithium diffusion coefficients

| Annealing temperature (K) | Annealing duration (h) | Lithium diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) |
|---------------------------|------------------------|--|
| 623 | 200 | $(7.8 \pm 0.31) \times 10^{-14}$ |
| 673 | 200 | $(4.4 \pm 0.17) \times 10^{-14}$ |
| 723 | 200 | $(1.0 \pm 0.04) \times 10^{-13}$ |
| 773 | 200 | $(1.8 \pm 0.07) \times 10^{-13}$ |
| 823 | 100 | $(1.4 \pm 0.05) \times 10^{-13}$ |
| 923 | 100 | $(1.7 \pm 0.07) \times 10^{-13}$ |
| 1023 | 100 | $(5.5 \pm 0.2) \times 10^{-13}$ |
| 1123 | 50 | $(1.05 \pm 0.04) \times 10^{-12}$ |
| 1123 | 50 | $(1.0 \pm 0.03) \times 10^{-12}$ |

homogeneous in the pellets. Moreover, the temperature in the B_4C pellets is uniform and below 600°C . The irradiation lasted two months and a total of about $25 \times 10^{20} \text{ }^{10}\text{B}$ atoms were burned per cm^3 , which represents a lithium concentration of approximately 2% (atomic). The nuclear microprobe is used to measure the lithium concentration with a quite good accuracy ($\pm 5\%$). The principle of this measure presented in a previous work [5]. Compared to other methods (ionic chromatography), this method does not require the setting in solution of the samples. This point is important because lithium atoms can easily volatilize during the alkaline attack in order to set the B_4C in solution.

After the irradiation, the pellets have been cut in discs of about 1 mm in thickness. In order to estimate the lithium diffusion coefficient, we performed isothermal annealing in a 1 Pa vacuum atmosphere for annealing temperatures in the temperature range 623–1123 K (cf. Table 1). Then these discs have been cut along the radial direction and the fresh surfaces have been polished in order to measure the lithium concentration.

3. Results and discussion

The amount of lithium lost during these annealing can be connected to the coefficient of diffusion by the classical diffusion equation. The geometrical ratio ts/D (thickness over diameter) of each pellet is about 1/7, this geometrical characteristic allows us to use the classical one-dimensional diffusion equation (cf. Fig. 1). Pumping during the annealing insures that the lithium concentration at the surface of the samples can be taken equal to zero. In other words, desorption effects at free surfaces of samples are neglected.

The diffusion equation can then be written as

$$D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}, \quad (1)$$

where c is the lithium concentration, D is the lithium diffusion coefficient. The boundary conditions of this equation can be written as

$$c(0, x) = c_0,$$

$$c(t, ts) = 0,$$

$$c(t, 0) = 0,$$

where c_0 is the uniform lithium concentration produced during the neutron irradiation. In this case, it is possible to deduce the lithium diffusion coefficient from the following equation:

$$\frac{Q(t)}{Q_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2 (2n+1)^2} \exp\left(\frac{-(2n+1)^2 Dt}{ts^2}\right), \quad (2)$$

where Q_0 is the amount of lithium atoms in the sample at the beginning of the annealing, $Q(t)$ the amount of lithium atoms in the sample at the end of the annealing and D is the lithium diffusion coefficient for an annealing temperature T . The knowledge of the amount $Q(t)/Q_0$ allows an iterative process in order to determine the value of D for each annealing temperature. Fig. 1 shows the evolution of the lithium diffusion coefficient as a function of the annealing temperature. Many analysis have been done to fit data by an Arrhenius law.

- Data are fitted by a linear regressions. The linear regression coefficient is equal to 0.71.
- Data are fitted by two linear regressions. The temperature of 823 K shares the two temperature ranges.

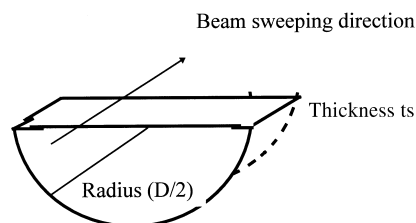


Fig. 1. Schematic description of the experiment. The nuclear microprobe proton beams sweeps irradiated B_4C samples along the thickness of the disc in order to determine the lithium concentration profiles.

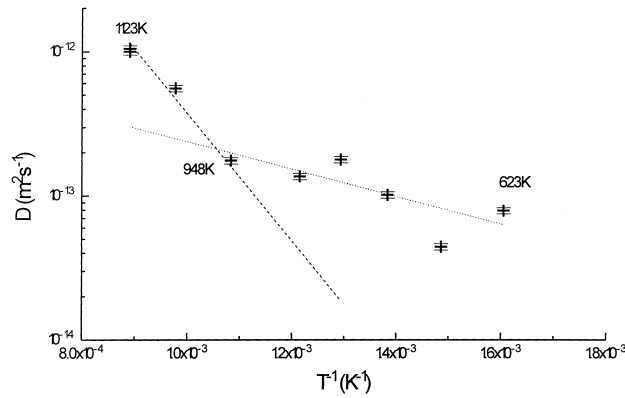


Fig. 2. Temperature dependence of the lithium diffusion coefficient in a dense boron carbide material. The dotted lines refer to the linear regression curves. The linear regression coefficients are respectively equal to 0.89 for the first regression (Eq. (3)) and 0.92 for the second one (Eq. (4)).

Linear regression coefficients were equal to 0.51 and 0.53.

- At last, data were fitted by two linear regressions with a different temperature (948 K) sharing the two temperature ranges. This fit gives the best linear regression coefficients (0.89 and 0.93).

Two linear regressions, with different slopes, on the experimental points allow to express the Arrhenius law for the lithium diffusion coefficients (see Fig. 2):

$$D(T) = 2.16 \times 10^{-12} \exp\left(-\frac{0.19}{k_B T}\right) \text{ m}^2/\text{s}, \quad (3)$$

where the activation energy E_a is equal to 0.19 eV for temperatures below 948 K and where k_B is the Boltzmann constant equal to $8.625 \times 10^{-5} \text{ eV K}^{-1}$.

$$D(T) = 1.01 \times 10^{-8} \exp\left(-\frac{0.88}{k_B T}\right) \text{ m}^2/\text{s}, \quad (4)$$

where the activation energy E_a is equal to 0.88 eV for temperatures above 948 K.

The presence of two straight lines on this curve could be interpreted as the evidence of two diffusion processes. Firstly for $948 \text{ K} < T < 1123 \text{ K}$ relates to the bulk diffusion in the grain; and secondly, for $948 \text{ K} > T > 623 \text{ K}$, relates to the diffusion in short-circuits which could be the grain boundaries. According to Harisson [7], it is possible to define different diffusion

processes only taking into account the migration of lithium atoms in grains and in the grains boundaries. If we note g as the grain size (10 μm) and δ as the grain boundary size (20 nm) and if we use the Eq. (4) to describe the lithium diffusion coefficient in the grain $D_{Li}(T)$, two parameters A and B can be defined:

$$A(T) = \frac{\sqrt{D_{Li}(T)t}}{g}, \quad (5)$$

$$B(T) = \frac{20\sqrt{D_{Li}(T)t}}{\delta}, \quad (6)$$

where t is the annealing time associated to each temperature T .

If at low temperature, $A(T)$ is superior to one, the bulk can be considered as homogeneous and the Fick equations can be applied. According to Hart [8], the lithium diffusion coefficient at low temperature depends on lithium diffusion coefficient in grains and in grain boundary.

If at low temperature, $B(T)$ is inferior to one, the lithium diffusion in the grain can be neglected.

Calculations (cf. Table 2) show that at low temperature (inferior to 948 K) $A(T)$ and $B(T)$ are always superior to one. Then the lithium coefficient diffusion measured at low temperature depends on the lithium diffusion coefficient in the grain and in the grain boundary.

Table 2
Calculations of the coefficients $A(T)$ and $B(T)$

| Temperature (K) | $D_{Li}(T) \text{ ms}^{-2} (\times 10^{-15})$ | Time (h) | $A(T)$ | $B(T)$ |
|-----------------|---|----------|--------|------------------|
| 623 | 0.77 | 200 | 2.35 | $2.1 \cdot 10^4$ |
| 673 | 2.60 | 200 | 4.33 | $2.3 \cdot 10^4$ |
| 723 | 7.43 | 100 | 5.17 | $2.5 \cdot 10^4$ |
| 773 | 18.52 | 100 | 8.16 | $4.0 \cdot 10^4$ |

Therefore, it must be pointed out in this assumption that nothing ensures that the lithium diffusion coefficient derived from Eq. (4) is the lithium diffusion coefficient in a grain of B_4C .

A similar form for the curve of the lithium diffusion coefficient versus annealing temperature was achieved by a previous work [6]. However, the lithium diffusion coefficients measured by the nuclear microprobe method are two orders of magnitude smaller than the previous ones [6]. The use of irradiated B_4C samples may explain such a difference. Kervalishvili deposited lithium atoms by spray coating on one end face of the cylindrical sample. The migration of lithium atoms in the B_4C samples may be ensured only by a grain boundary diffusion even at high annealing temperatures. In our experiment, lithium atoms are generated in grains and the diffusion in grains always exists. Moreover, damages induced by neutron irradiation in B_4C change the crystallographic structure of the rhombohedral unit cell and then the microscopic motion of lithium atoms in the B_4C lattice. A previous work [9] has shown that under neutron irradiation, the linear CBC chains linking icosahedra in the B_4C structure vanish. Knocked atoms belonging to these destroyed CBC chains relax in interstitial positions and may close some lithium diffusion paths in the grain.

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